

Final Report for Period: 01/2009 - 08/2009**Submitted on:** 11/22/2009**Principal Investigator:** El-Sayed, Mostafa A.**Award ID:** 0527297**Organization:** GA Tech Res Corp - GIT**Submitted By:**

El-Sayed, Mostafa - Principal Investigator

Title:

Radiative and Ultrafast Non-radiative Electronic Relaxation in Individual and Assembled Noble Metallic Nanoparticles of Different Shapes

Project Participants**Senior Personnel****Name:** El-Sayed, Mostafa**Worked for more than 160 Hours:** Yes**Contribution to Project:****Post-doc****Graduate Student****Undergraduate Student****Technician, Programmer****Other Participant****Research Experience for Undergraduates****Organizational Partners****Other Collaborators or Contacts**

no other collaborators

Activities and Findings**Research and Education Activities:**

Twenty five papers have been published and two students were trained on Electron Beam Lithography which is important in making well defined nanoparticle assemblies. This is required to carry out our research on the effect of coupling between nanoparticles on their non-radiative and radiative properties. The programs needed for making different structures have been developed, including designs for discs, prisms, rods, and rings. STUDENTS got trained in conjugating gold nano-particle to biological systems. In addition, several students were trained in theoretical computations on plasmonic particles using the DDA method. From these computations, predictions regarding the inter-particle coupling has been calculated and new interesting results are being calculated.

A postdoctoral fellow, Dr Svetlana Neretina was trained in this area well and became an expert in this field of nano-technology and solar energy conversion. As a result, She was offered and accepted an Assistant professorship at the engineering department of Temple University.

This Last year I have accepted to sponsor a young lady who failed the Literature Exams and was asked to leave GT. I realized that she is very good in creative research. She retook the Exams and passed them and is doing excellent research.

Findings: (See PDF version submitted by PI at the end of the report)

- 1.) Photothermal reshaping of prismatic gold nanoparticles in periodic monolayer arrays by femtosecond laser pulses: Prismatic gold nanoparticles in the periodic monolayer arrays prepared with nanosphere lithography technique can be reshaped with femtosecond laser pulses at different powers and wavelengths. As the power density of the 400nm femtosecond laser pulse increases, the prismatic particle tips begin to round and the overall particle shape changes from a prism to a sphere with a tripodal intermediate. From the results of this work, it is shown that by changing the wavelength and power density of the femtosecond laser pulse, one can control the final shape of the particles formed from the original prismatic nanoparticles.
- 2.) The optically detected coherent lattice oscillations in silver and gold monolayer periodic nanoprisms arrays: The Au nanoprisms formed by this method are found to have sharper tips than the corresponding Ag nanoprisms. For both Au and Ag nanoparticles, the surface plasmon absorption maximum is found to depend linearly on size. The coherent lattice oscillation periods are also found to follow the calculated dependence, the Au nanoparticle deviates from this model, and the deviation is found to increase with the size of the nanoparticles. This deviation can be explained by considering interparticle coupling that is sensitive to the sharpness of the nanoprism tips, which is less for Ag.
- 3.) Ultrafast cooling of photoexcited electrons in gold nanoparticle-thiolated DNA conjugates involves the dissociation of the gold-thiol bond: It is found that femtosecond pulse excitation of the DNA-modified nanoparticles at a wavelength of 400nm leads to desorption of the thiolated DNA strands from the nanoparticle surface by the dissociation of the gold-sulfur bond. The laser-initiated gold-sulfur bond-breaking process is a new pathway for non-radiative relaxation of the optically excited electrons within the DNA-modified gold nanoparticles, as manifested by a faster decay rate of the excited electronic distribution at progressively higher laser pulse energies.
- 4.) Size-dependent ultrafast electronic energy relaxation and enhanced fluorescence of copper nanoparticles: The energy relaxation of the electrons in the conduction band of 12 and 30 nm diameter copper nanoparticles in colloidal solution was investigated using femtosecond time-resolved transient spectroscopy. Experimental results show that the hot electron energy relaxation is faster in 12 nm copper nanoparticles (0.37 ps) than that in 30 nm copper nanoparticles (0.51 ps), which is explained by the size-dependent electron-surface phonon coupling. Additional mechanisms involving trapping or energy transfer processes to the denser surface states (imperfection) in the smaller nanoparticles are needed to explain the relaxation rate in the 12 nm nanoparticles.
- 5.) Supported gold nanoparticle propulsion from support surface fueled by absorption of femtosecond laser pulse at their surface plasmon resonance: We report on the observation that, when femtosecond laser pulses in resonance with the strong surface plasmon oscillations are used for excitation, the rates of absorption and heating become faster than the rate of melting of the nanoparticle. The nanoprism is observed to fly away with jet velocities while preserving its shape in both air and liquid media. Using SEM and AFM techniques, two propulsion mechanisms were described, one for the gaseous environment and one for the liquid environment. In air, a rapid atomic sublimation of the metallic particle surface results in a rapid build up of an ultrahigh gold atomic pressure underneath the prism, which enables it to fly. In liquid, the substrate-bound nanoparticle ejection requires less than one tenth of the energy required in air, and an propulsion mechanism was suggested that involves energy transfer from the photo-excited nanoprism to the solvent within cavities and defects at the particle-substrate interface. The hot-solvent molecules result in an intense pressure at the particle-substrate interface, resulting in particle ejection.
- 6.) Effect of the lattice crystallinity on the electron-phonon relaxation rates in gold

nanoparticles: We have found that the electron-phonon relaxation rate decreases greatly when polycrystalline prismatic gold nanoparticles are annealed and transformed into nearly single-crystalline nanospheres. The results are explained by the presence of high density grain boundaries with dense, high-frequency molecular type vibrations which are effective in removing the energy of the excited electrons in the polycrystalline prismatic nanoparticles.

7.) The effect of plasmon field on the coherent lattice phonon oscillation in electron beam nanofabricated gold particle pairs: We found that the fractional shift in the coherent lattice phonon oscillation frequency follows an exponential decay with respect to the inter-particle gap scaled by the disc diameter with the same decay constant as that previously observed for the fractional shift in the surface plasmon electronic oscillation resonance frequency. This strongly suggests that it is the near-field coupling between the particles that shifts both the coherent electronic oscillation (plasmon) frequency and the coherent lattice oscillation (phonon) frequency.

In the area of understanding the localized surface plasmon resonance properties of metal nanoparticles and their assemblies we have published 11 articles and made the following contributions:

8.) Aspect ratio dependence of the enhanced fluorescence intensity of gold nanorods: experimental and simulation study: The calculation of the fluorescence spectra requires knowledge of the nanorod size distribution, the enhancement factors, and the shape of the unenhanced fluorescence spectrum. The size distribution is determined from the fit of the observed absorption spectrum for each aspect ratio studied to the theoretical model of Gans. A comparison between the observed and the calculated fluorescence band shapes was found to be good.

9.) Gold and silver nanoparticles in sensing and imaging: sensitivity of plasmon response to size, shape, and metal composition: We investigated the dependence of the sensitivity of the surface plasmon resonance (frequency and bandwidth) response to changes in their surrounding environment and the relative contribution of optical scattering to the total extinction, on the size and shape of nanorods and the type of metal, Au or Ag. The spectral sensitivity has two controlling factors: first the bulk plasma wavelength, a property dependent on the metal type, and second on the aspect ratio of the nanorods which is a geometrical parameter. It is found that the sensitivity is linearly proportional to both these factors. The insensitivity of the plasmon response to the metal composition is attributable to the fact that the bulk plasma frequency of the metal has a similar value for the noble metals. Furthermore, Ag nanorods have an additional advantage as better scatterers compared with Au nanorods of the same size.

10.) Plasmon coupling in nanorod assemblies: optical absorption, discrete dipole approximation simulation, and exciton-coupling model: The shape anisotropy of nanorods gives rise to two distinct orientational modes by which nanorods can be assembled ? end-to-end and side-by-side ? analogous to the well-known H and J aggregates in organic chromophores. Optical absorption spectra of gold nanorods have earlier been observed to show a red-shift of the longitudinal plasmon band for the end-to-end linkage of nanorods, resulting from the plasmon coupling between neighboring nanoparticles, similar to the assembly of gold nanospheres. We observe that side-by-side linkage of nanorods in solution shows a blue-shift of the longitudinal plasmon band and a red-shift of the transverse plasmon band, which showed good agreement with the calculated optical spectra of the nanorod dimers using the DDA method. The strength of plasmon coupling was seen to increase with decreasing inter-nanorod distance and an increase in the number of interacting nanorods.

11.) On the scaling behavior of the distance decay length of plasmon coupling in metal nanoparticle pairs: Localized surface plasmon resonances (LSPRs) in lithographically fabricated gold nanodisc pairs were investigated using microabsorption spectroscopy and electrodynamic simulations. In agreement with previous work, we found that the fractional plasmon wavelength shift for polarization along the interparticle axis decays nearly exponentially with the interparticle gap. In addition, by determining the exponential decay

parameters, the decay length and the amplitude, in units of the particle size (decay length) and fractional plasmon shift (amplitude), we were able to derive a 'plasmon ruler equation' that estimates the interparticle separation between two gold nanospheres in a biological system via the observed fractional shift of the plasmon band. We found good agreement of the interparticle separations estimated using this equation with the experimental observations of Reinhard et al. (Nano Lett. 2005, 5, 2246).

In the area of energy and electron transport in semiconductor nanostructures, we have published 4 articles and made the following contributions:

12.) Observation of optical gain in solutions of CdS quantum dots at room temperature in the blue region: We were able to obtain the first optical gain from quantum dots (CdS nanodots) in liquid solution at room temperatures. These results suggest that CdS quantum dots in solution are excellent gain media for optically pumped high power blue lasers.

13.) Ultrafast electronic relaxation and charge-carrier localization in CdS/CdSe/CdS quantum-dot quantum-well heterostructures: The relaxation and localization times of excited electrons in CdS/CdSe/CdS colloidal quantum wells were measured using sub-picosecond spectroscopy. Two-component rise times in the stimulated emission are attributed to intraband relaxation of carriers generated directly within the CdSe well (fast component) and charge transfer of core-localized carriers across the CdS/CdSe interface (slow component). This is the first reported observation of simultaneous photon absorption in the core and well of a quantum-dot heterostructure.

14.) Charge in titania structure from amorphous to crystalline increasing photoinduced electron-transfer rate in dye-titania systems: Thin titania gel films containing well-dispersed fluorescein dye were prepared by the sol-gel method and treated with steam to promote crystal growth of the titania particles. It is known that steam treatment converts the titania structure from amorphous to crystalline. In the present study, such change is found to increase the rate of the photo-induced electron transfer from and to dispersed fluorescein dye molecules.

15.) Plasmon field effects on non-radiative relaxation processes in composite metal semiconductor nanostructures: Using a metal / semiconductor nanostructure composed of CdTe nanowires coated in a thin nanoshell of gold, we found that the intense induced electromagnetic field of plasmonic nanostructures has a significant effect on the non-radiative electron processes of semiconductor CdTe nanowires when the two materials are in contact with one another. The intense plasmonic fields that have been well documented to enhance radiative processes in the near-field vicinity were also shown to enhance non-radiative relaxation processes of quantized electronic excitations and some mechanisms for this result were postulated that are the result of enhancing the radiative processes themselves.

We also found that the plasmonic field of the nano-shell can be polarized or unpolarised depending on the thickness of the shell.
thickness but un-polarized at thick shell thickness .

Training and Development:

The graduate students were trained in the field of electron beam Lithography, femtosecond laser operation as well as doing DDA computations and simulations. This is in addition to be trained in the field of imaging like TEM, SEM and AFM. All these fields are very important to the scientists and engineers in the field of Nano-Technology.

TRAINING IN COMPUTATION has been accomplished for three students.

One of our postdoctoral students, Dr Svetlana Neretina has been offered and accepted the position of assistant professor in Temple U Engineering department. One of our graduated Ph D students accepted a Postdoctoral position at the Air Force Research Labs at Dayton, Oh.

Outreach Activities:

I gave several talks about nano-technology to investment groups and a number of campus wide special named public lectures to general audiences on this topic.

I gave several talks at universities and couple of high schools and to a senior citizen group in Atlanta.

I gave a popular talk about Nano-technology at the Georgia section of ACS.

Journal Publications

Darugar, Qusai;Qian, Wei;El-Sayed, Mostafa A.;, "Observation of optical gain in solutions of CdS quantum dots at room temperature in the blue region", Applied Physics Letters, p. 261108/1-, vol. 88, (2006). Published,

Darugar, Qusai;Qian, Wei;El-Sayed, Mostafa A.;Pileni, Marie-Paule;, "Size-Dependent Ultrafast Electronic Energy Relaxation and Enhanced Fluorescence of Copper Nanoparticles", Journal of Physical Chemistry B, p. 143-149, vol. 110, (2006). Published,

Eustis, Susie;El-Sayed, Mostafa;, "Aspect Ratio Dependence of the Enhanced Fluorescence Intensity of Gold Nanorods: Experimental and Simulation Study", Journal of Physical Chemistry B, p. 16350-163, vol. 109, (2005). Published,

Eustis, Susie;Hsu, Hsan-Yin;El-Sayed, Mostafa A.;, "Gold Nanoparticle Formation from Photochemical Reduction of Au³⁺ by Continuous Excitation in Colloidal Solutions. A Proposed Molecular Mechanism", Journal of Physical Chemistry B, p. 4811-4815, vol. 109, (2005). Published,

Eustis, Susie;Krylova, Galina;Eremenko, Anna;Smirnova, Natalie;Schill, Alexander W.;El-Sayed, Mostafa;, "Growth and fragmentation of silver nanoparticles in their synthesis with a fs laser and CW light by photosensitization with benzophenone", Photobiological Sciences, p. 154-159, vol. 4, (2005). Published,

Huang, Wenyu;Qian, Wei;El-Sayed, Mostafa A.;, "Photothermal reshaping of prismatic Au nanoparticles in periodic monolayer arrays by femtosecond laser pulses", Journal of Applied Physics, p. 114301/1-, vol. 98, (2005). Published,

Huang, Wenyu;Qian, Wei;El-Sayed, Mostafa A.;, "The Optically Detected Coherent Lattice Oscillations in Silver and Gold Monolayer Periodic Nanoprism Arrays: The Effect of Interparticle Coupling", Journal of Physical Chemistry B, p. 18881-188, vol. 109, (2005). Published,

Huang, Wenyu;Qian, Wei;El-Sayed, Mostafa A.;, "Gold Nanoparticles Propulsion from Surface Fueled by Absorption of Femtosecond Laser Pulse at Their Surface Plasmon Resonance", Journal of the American Chemical Society, p. 13330-133, vol. 128, (2006). Published,

Huang, Wenyu;Qian, Wei;El-Sayed, Mostafa A.;, "Gigahertz optical modulation resulting from coherent lattice oscillations induced by femtosecond laser pumping of 2D photonic crystals of gold-capped polystyrene microspheres", Advanced Materials (Weinheim, Germany), p. 733-737, vol. 20, (2008). Published,

Huang, Wenyu;Qian, Wei;El-Sayed, Mostafa A.;Ding, Yong;Wang, Zhong Lin;, "Effect of Lattice Crystallinity on the Electron-Phonon Relaxation Rates in Gold Nanoparticles", Journal of Physical Chemistry C, p. 10751-107, vol. 111, (2007). Published,

Huang, Wenyu;Qian, Wei;Jain, Prashant K.;El-Sayed, Mostafa A.;, "The Effect of Plasmon Field on the Coherent Lattice Phonon Oscillation in Electron-Beam Fabricated Gold Nanoparticle Pairs", Nano Letters, p. 3227-3234, vol. 7, (2007). Published,

Jain, Prashant K.;El-Sayed, Mostafa A.;, "Surface Plasmon Resonance Sensitivity of Metal Nanostructures: Physical Basis and Universal Scaling in Metal Nanoshells", Journal of Physical Chemistry C, p. 17451-174, vol. 111, (2007). Published,

Jain, Prashant K.;El-Sayed, Mostafa A.;, "Universal Scaling of Plasmon Coupling in Metal Nanostructures: Extension from Particle Pairs to Nanoshells", Nano Letters, p. 2854-2858, vol. 7, (2007). Published,

- Jain, Prashant K.;El-Sayed, Mostafa A.;, "Surface Plasmon Coupling and Its Universal Size Scaling in Metal Nanostructures of Complex Geometry: Elongated Particle Pairs and Nanosphere Trimers", *Journal of Physical Chemistry C*, p. 4954-4960, vol. 112, (2008). Published,
- Jain, Prashant K.;Eustis, Susie;El-Sayed, Mostafa A.;, "Plasmon Coupling in Nanorod Assemblies: Optical Absorption, Discrete Dipole Approximation Simulation, and Exciton-Coupling Model", *Journal of Physical Chemistry B*, p. 18243-182, vol. 110, (2006). Published,
- Jain, Prashant K.;Huang, Wenyu;El-Sayed, Mostafa A.;, "On the Universal Scaling Behavior of the Distance Decay of Plasmon Coupling in Metal Nanoparticle Pairs: A Plasmon Ruler Equation", *Nano Letters*, p. 2080-2088, vol. 7, (2007). Published,
- Jain, Prashant K.;Qian, Wei;El-Sayed, Mostafa A.;, "Ultrafast Cooling of Photoexcited Electrons in Gold Nanoparticle-Thiolated DNA Conjugates Involves the Dissociation of the Gold-Thiol Bond", *Journal of the American Chemical Society*, p. 2426-2433, vol. 128, (2006). Published,
- Jain, Prashant K.;Qian, Wei;El-Sayed, Mostafa A.;, "Ultrafast Electron Relaxation Dynamics in Coupled Metal Nanoparticles in Aggregates", *Journal of Physical Chemistry B*, p. 136-142, vol. 110, (2006). Published,
- Lee, Kyeong-Seok;El-Sayed, Mostafa A.;, "Dependence of the Enhanced Optical Scattering Efficiency Relative to That of Absorption for Gold Metal Nanorods on Aspect Ratio, Size, End-Cap Shape, and Medium Refractive Index", *Journal of Physical Chemistry B*, p. 20331-203, vol. 109, (2005). Published,
- Lee, Kyeong-Seok;El-Sayed, Mostafa A.;, "Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition", *Journal of Physical Chemistry B*, p. 19220-192, vol. 110, (2006). Published,
- Mahmoud, M. A.;El-Sayed, M. A.;, "Comparative Study of the Assemblies and the Resulting Plasmon Fields of Langmuir-Blodgett Assembled Monolayers of Silver Nanocubes and Gold Nanocages", *Journal of Physical Chemistry C*, p. 14618-146, vol. 112, (2008). Published,
- Neretina, Svetlana;Qian, Wei;Dreaden, Erik;El-Sayed, Mostafa A.;Hughes, Robert A.;Preston, John S.;Mascher, Peter;, "Plasmon Field Effects on the Nonradiative Relaxation of Hot Electrons in an Electronically Quantized System: CdTe-Au Core-Shell Nanowires", *Nano Letters*, p. 2410-2418, vol. 8, (2008). Published,
- Nishikiori, Hiromasa;Qian, Wei;El-Sayed, Mostafa A.;Tanaka, Nobuaki;Fujii, Tsuneo;, "Change in Titania Structure from Amorphousness to Crystalline Increasing Photoinduced Electron-Transfer Rate in Dye-Titania System", *Journal of Physical Chemistry C*, p. 9008-9011, vol. 111, (2007). Published,
- Tabor, Christopher;Qian, Wei;El-Sayed, Mostafa A.;, "Dependence of the Threshold Energy of Femtosecond Laser Ejection of Gold Nanoprisms from Quartz Substrates on the Nanoparticle Environment", *Journal of Physical Chemistry C*, p. 8934-8941, vol. 111, (2007). Published,
- . Jain, Prashant K.; El-Sayed, Mostafa A.. (), (12), -4352, "Noble Metal Nanoparticle Pairs: Effect of Medium for Enhanced Nanosensing.", *Nano Letters*, p. 4347, vol. 8, (2008). Published,
- . Mahmoud, M. A.; El-Sayed, M. A., " Comparative Study of the Assemblies and the Resulting Plasmon Fields of Langmuir-Blodgett Assembled Monolayers of Silver Nanocubes and Gold Nanocages", *Journal of Physical Chemistry C*, p. 14618, vol. 112, (2008). Published,
- . Neretina, Svetlana; Qian, Wei; Dreaden, Erik; El-Sayed, Mostafa A.; Hughes, Robert A.; Preston, John S.; Mascher, Peter., ". Plasmon Field Effects on the Nonradiative Relaxation of Hot Electrons in an Electronically Quantized System: CdTe-Au Core-Shell Nanowires", *nano-letter*, p. 2410, vol. 8, (2008). Published,

Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

1. Extending our Knowledge in the field of Nanotechnology
2. We have evaluated, theoretically and experimentally, the use of nano-technology in the fields of :
 - a. Sensors , and,
 - b. Imaging, and,
 - c. Photo thermal Applications and
 - d. nano-photonics

Contributions to Other Disciplines:

May be as we find new applications of nanoscience in nanotechnology , specially in: the sensor field as well as medical Diagnosis and photo-thermal Therapy. Our demonstrating that gold and silver nanoparticles have such large enhanced optical properties lead to their potential use in medical diagnoses . We have ,in other studies, shown that their photo-thermal properties studied in the DMR program has the potential use in cancer photo-thermal therapy.

Contributions to Human Resource Development:

We have supervised and trained one NNIN undergraduate engineer student who is now applying to engineering graduate schools and one undergraduate student in science who has recently joined the group as a first year graduate student in chemistry. This is besides the training of three graduate students in Nano-Technology.

Contributions to Resources for Research and Education:

One of my students, Susie Eustis, developed a new simple method to make gold and silver nanoparticles based on simple chemical principles which she wrote and sent to the J Chemical Education for undergraduate lab experiment.

Contributions Beyond Science and Engineering:

I am working with a scientist from a company who has an NSF grant to develop a far IR source to detect scattering from biological molecules labeled with gold or silver nanoparticles. If it works, It can be used in cancer in-Vivo detection.

Conference Proceedings

Categories for which nothing is reported:

Organizational Partners

Any Book

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Any Product

Any Conference

2005

1. Huang, Wenyu; Qian, Wei; El-Sayed, Mostafa A., "Photothermal reshaping of prismatic Au nanoparticles in periodic monolayer arrays by femtosecond laser pulses," *Journal of Applied Physics*, 98 (11), 114301/1-114301/8, (2005).

Abstract: Prismatic gold nanoparticles in the periodic monolayer arrays prepared with nanosphere lithography technique can be reshaped with femtosecond laser pulses at different powers and wavelengths. As the power density of 400 nm femtosecond laser increases, the prismatic particle tips begin to round and the overall particle shape changes from a prism to a sphere with a tripodal intermediate. The formation of the tip-rounded nanoprisms is probably due to the dewetting properties of gold on quartz surface and the low melting temperature at the tips. The formation of the tripodal nanoparticles is attributed to the inhomogeneous heating and lattice rearrangement of the as-deposited nanoparticles to a metastable state, which is more stable than the prismatic shape but less stable than the spherical shape. With 800 nm femtosecond laser irradiation, only tip-rounded nanoprisms are observed and no spherical nanoparticles are formed at the laser powers used. This is most likely due to the blueshift of the plasmon absorption band for the transformed particles, so that they cannot absorb the required energy to overcome the barrier to make the spherical shape. With 700 nm femtosecond laser irradiation, the tip-rounded and the tripodal nanoparticles are formed and few spherical particles are observed at the higher laser power density. From the results of this work, it is shown that by changing the wavelength and power density of the femtosecond laser, one can control the final shape of the particles formed from the original prismatic nanoparticles.

2. Huang, Wenyu; Qian, Wei; El-Sayed, Mostafa A., "The optically detected coherent lattice oscillations in silver and gold monolayer periodic nanoprism arrays: The effect of interparticle coupling," *Journal of Physical Chemistry B*, 109 (40), 18881-18888, (2005).

Abstract: Using femtosecond transient spectroscopy, we studied the optically detected laser-induced coherent phonon oscillation of monolayers of periodic arrays of prismatic-shaped silver and gold nanoparticles, assembled by using the technique of nanosphere lithography. In this method, the same size of polystyrene sphere and the same vacuum conditions are used. Under these circumstances, the gold nanoprisms formed are found to have sharper tips than the corresponding silver nanoprisms. For both gold and silver nanoparticles, the surface plasmon absorption maximum is found to depend linearly on size. The coherent lattice oscillation periods are also found to depend linearly on size. However, although the observed dependence for the silver nanoparticle is found to follow the calculated dependence of a single particle on size (based on a one-dimensional standing wave model), the gold nanoparticle deviates from this model, and the deviation is found to increase with the size of the nanoparticles. This deviation can be explained by considering interparticle coupling. A simple interparticle lattice oscillating dipolar coupling model of the dimer is found to qualitatively account for both the sign and the

size dependence of the deviation. The absence of this deviation in the silver nanoparticle arrays is blamed on the weak interparticle coupling due to their rounded tips and the possibility of oxidation of their surfaces.

3. Kyeong-Seok Lee and Mostafa A. El-Sayed, "Dependence of the enhanced optical scattering efficiency relative to that of absorption for gold metal nanorods on aspect ratio, size, end-cap shape, and medium refractive index," *Journal of Physical Chemistry B*, 109 (43), 20331-20338, (2005).

Abstract: The current intense interest in the properties of plasmonic nanostructures for their applications in chemical and biochemical sensors, medical diagnostics and therapeutics, and biological imaging is fundamentally based on their enhanced optical absorption and scattering properties. In this study, the optical extinction, absorption, and scattering efficiencies were calculated as a function of shape definition, aspect ratio, surrounding medium, and material selection. The discrete dipole approximation method was used, which is known to be a very useful and versatile computational tool for particles with any arbitrary shape. Relative contribution of scattering to the total extinction for the longitudinal mode was found to be significantly dependent on the aspect ratio of the nanorod in a somewhat complex manner, different from a typical linear relationship for the resonance wavelength. A slight elongation of Au nanosphere gives rise to a drastic increase in the relative scattering efficiency, which eventually reaches a maximum and begins to decrease with further increase in the aspect ratio. This is ascribed to the increasing absorptive contribution from the larger imaginary dielectric function of the metal particle in the longer wavelength region where the red-shifted excitation of the longitudinal resonance mode occurs. For transverse mode exhibiting the blue-shift in the resonance peak, on the contrary, the absorption efficiency is relatively enhanced compared to the scattering efficiency with increasing aspect ratio. This is thought to result from the dominant effect of the interband transition present in this wavelength region. Besides the dependence of plasmonic characteristics on the aspect ratio of nanorod, the DDA results for a small change of the end-cap shape and the index of the surrounding medium lead us to conclude that there exist two competing key factors: a weighting factor assigned to the shape parameter and the dielectric function of the metal particle, which control the relative enhancement in the scattering and absorption as well as the linearity of resonance wavelength with regard to the aspect ratio.

4. Susie Eustis and Mostafa El-Sayed, "Aspect Ratio Dependence of the Enhanced Fluorescence Intensity of Gold Nanorods: Experimental and Simulation Study," *Journal of Physical Chemistry B*, 109 (34), 16350-16356 (2005).

Abstract: Experimental observations and theoretical treatments are carried out for the band shape and relative intensity of the emission from gold nanorods of various aspect ratios in the range between 2.25 (1.5 theory) and 6.0 (9 theory). The calculation of the fluorescence spectra requires knowledge of the nanorod size distribution, the enhancement factors, and the shape of the unenhanced fluorescence spectrum. The size distribution is determined from the fit of the observed absorption spectrum for each value

of aspect ratio studied to the theoretical model of Gans. The theory by Boyd and Shen is used for calculating the enhancement of the fluorescence spectrum of the previously observed weak emission of bulk gold, which originates from the interband transition. This is carried out for nanorods of different aspect ratios. To compare theory to the observed nanorod fluorescence spectra, which suffer from self-absorption, the calculated nanorod fluorescence spectra are corrected for this effect using the observed absorption spectra. The comparison between the observed and the calculated fluorescence band shapes is found to be good. The calculated changes in the relative intensities upon changing the aspect ratios are found to be much greater than that observed. This is due to the fact that for the observed emission of all the nanorods studied nonradiative processes dominate the relaxation mechanism of the excited state, a fact that was not included in the theoretical treatments.

5. Susie Eustis, Hsan-Yin Hsu, and Mostafa A. El-Sayed, "Gold Nanoparticle Formation from Photochemical Reduction of Au^{3+} by Continuous Excitation in Colloidal Solutions. A Proposed Molecular Mechanism," *Journal of Physical Chemistry B*, 109, 11, 4811-4815, (2005).

Abstract: A photochemical reduction of Au^{3+} with continuous 250-400 nm excitation is studied in ethylene glycol, and poly(vinylpyrrolidone) (PVP) is used as a capping material. After the absorption of Au^{3+} disappears, excitation is stopped. The surface plasmon absorption of gold as well as the thermal reappearance of the Au^{3+} absorption are found to increase as a function of time. The rates of these changes are studied as a function of the mole fraction of ethylene glycol in water. Experimental results show that a small amount of ethylene glycol increases the formation of gold nanoparticles and decreases the reformation of the Au^{3+} absorption after irradiation. Increasing the glycol concentration first increases the rate of formation of gold nanoparticles to a maximum at a mole fraction 0.40. As the glycol concentration is further increased, the rate of formation of the gold nanoparticles and the rate of re-formation of Au^{3+} decrease. A mechanism is proposed that involves the reduction of the excited Au^{3+} to Au^{2+} by ethylene glycol. This is followed by the disproportionation of Au^{2+} to Au^{3+} and Au^{1+} . Both the reduction of Au^{1+} by ethylene glycol and its disproportionation lead to the formation of Au^0 , which upon nucleation and growth form Au nanoparticles.

6. Susie Eustis; Galina Krylova; Anna Eremenko; Natalie Smirnova; Alexander W. Schill; Mostafa El-Sayed, "Growth and Fragmentation of Silver Nanoparticles in their Synthesis with a fs Laser and CW Light by Photo-Sensitization with Benzophenone," *Photochemical & Photobiological Sciences*, 4, 154-159 (2005).

Abstract: The photo-sensitization synthetic technique of making silver nanoparticles using benzophenone is studied using both a laser and a mercury lamp as light sources. The power and irradiation time dependence of the synthesized nanoparticle absorption spectra and their size distribution [as determined by transmission electron microscopy (TEM)] are studied in each method and compared. In the laser synthesis, as either the laser power or the irradiation time increases, the intensity of the surface plasmon resonance absorption at 400 nm is found to increase linearly first, followed by a reduction

of the red edge of the plasmon resonance absorption band. The TEM results showed that in the laser synthesis low powers and short irradiation times produce nanoparticles around 20 nm in diameter. Increasing the power or irradiation time produces a second population of nanoparticles with average size of 5 nm in diameter. These small particles are believed to be formed from the surface ablation of the large particles. The surface plasmon absorption band is found to be narrower when the nanoparticles are produced with laser irradiation. Throughout the exposure time with the CW lamp, the plasmon resonance absorption band of the particles formed first grows in intensity, then blue shifts and narrows, and finally red shifts while decreasing in intensity. The TEM results for lamp samples showed particle formation and growth, followed by small nanoparticle formation. The above results are discussed in terms of a mechanism in which, the excited benzophenone forms the ketal radical, which reduces Ag^+ in solution and on the Ag nanoparticle surface. As the time of irradiation or the light energy increases the benzophenone is consumed, which is found to be the limiting reagent. This stops the formation of the normal large nanoparticles while their photo-ablation continues to make the small particles.

2006

1. Darugar, Qusai; Qian, Wei; El-Sayed, Mostafa A.; Pileni, Marie-Paule. "Size-Dependent Ultrafast Electronic Energy Relaxation and Enhanced Fluorescence of Copper Nanoparticles," *Journal of Physical Chemistry B*, 110 (1), 143-149, (2006).

Abstract: The energy relaxation of the electrons in the conduction band of 12 and 30 nm diameter copper nanoparticles in colloidal solution was investigated using femtosecond time-resolved transient spectroscopy. Experimental results show that the hot electron energy relaxation is faster in 12 nm copper nanoparticles (0.37 ps) than that in 30 nm copper nanoparticles (0.51 ps), which is explained by the size-dependent electron-surface phonon coupling. Additional mechanisms involving trapping or energy transfer processes to the denser surface states (imperfection) in the smaller nanoparticles are needed to explain the relaxation rate in the 12 nm nanoparticles. The observed fluorescence quantum yield from these nanoparticles is found to be enhanced by roughly 5 orders of magnitude for the 30 nm nanoparticles and 4 orders of magnitude for the 12 nm nanoparticles (relative to bulk copper metal). The increase in the fluorescence quantum yield is attributed to the electromagnetic enhancement of the radiative recombination of the electrons in the s-p conduction band below the Fermi level with the holes in the d bands due to the strong surface plasmon oscillation in these nanoparticles.

2. Prashant K. Jain; Wei Qian, Mostafa A. El-Sayed, "Ultrafast Electron Relaxation Dynamics in Coupled Metal Nanoparticles in Aggregates," *Journal of Physical Chemistry B*, 110 (1), 136-142, (2006).

Abstract: We report the effect of aggregation in gold nanoparticles on their ultrafast electron-phonon relaxation dynamics measured by femtosecond transient absorption pump-probe spectroscopy. UV-visible extinction and transient absorption of the solution-stable aggregates of gold nanoparticles show a broad absorption in the 550-700-nm

region in addition to the isolated gold nanoparticle plasmon resonance. This broad red-shifted absorption can be attributed to contributions from gold nanoparticle aggregates with different sizes and/or different fractal structures. The electron-phonon relaxation, reflected as a fast decay component of the transient bleach, is found to depend on the probe wavelength, suggesting that each wavelength interrogates one particular subset of the aggregates. As the probe wavelength is changed from 520 to 635 nm across the broad aggregate absorption, the rate of electron-phonon relaxation increases. The observed trend in the hot electron lifetimes can be explained on the basis of an increased overlap of the electron oscillation frequency with the phonon spectrum and enhanced interfacial electron scattering, with increasing extent of aggregation. The experimental results strongly suggest the presence of intercolloid electronic coupling within the nanoparticle aggregates, besides the well-known dipolar plasmon coupling.

3. Prashant K. Jain, Wei Qian and Mostafa A. El-Sayed, M. A. "Ultrafast Cooling of Photoexcited Electrons in Gold Nanoparticle-Thiolated DNA Conjugates Involves the Dissociation of the Gold-Thiol Bond," *Journal of the American Chemical Society*, 128 (7), 2426-2433, (2006).

Abstract: Using UV-visible extinction spectroscopy and femtosecond pump-probe transient absorption spectroscopy, we have studied the effect of femtosecond laser heating on gold nanoparticles attached to DNA ligands via thiol groups. It is found that femtosecond pulse excitation of the DNA-modified nanoparticles at a wavelength of 400 nm leads to desorption of the thiolated DNA strands from the nanoparticle surface by the dissociation of the gold-sulfur bond. The laser-initiated gold-sulfur bond-breaking process is a new pathway for nonradiative relaxation of the optically excited electrons within the DNA-modified gold nanoparticles, as manifested by a faster decay rate of the excited electronic distribution at progressively higher laser pulse energies. The experimental results favor a bond dissociation mechanism involving the coupling between the photoexcited electrons of the nanoparticles and the gold-sulfur bond vibrations over one involving the conventional phonon-phonon thermal heating processes. The latter processes have been observed previously by our group to be effective in the selective photothermal destruction of cancer cells bound to anti-epidermal growth factor receptor-conjugated gold nanoparticles.

4. Kyeong-Seok Lee and Mostafa A. El-Sayed, "Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition," *Journal of Physical Chemistry B*, 110(39), 19220-19225, (2006).

Abstract: Plasmonic metal nanoparticles have great potential for chemical and biological sensor applications, due to their sensitive spectral response to the local environment of the nanoparticle surface and ease of monitoring the light signal due to their strong scattering or absorption. In this work, we investigated the dependence of the sensitivity of the surface plasmon resonance (frequency and bandwidth) response to changes in their surrounding environment and the relative contribution of optical scattering to the total

extinction, on the size and shape of nanorods and the type of metal, that is, Au vs Ag. Theoretical consideration on the surface plasmon resonance condition revealed that the spectral sensitivity, defined as the relative shift in resonance wavelength with respect to the refractive index change of surrounding materials, has two controlling factors: first the bulk plasma wavelength, a property dependent on the metal type, and second on the aspect ratio of the nanorods which is a geometrical parameter. It is found that the sensitivity is linearly proportional to both these factors. To quantitatively examine the dependence of the spectral sensitivity on the nanorod metal composition and the aspect ratio, the discrete dipole approximation method was used for the calculation of optical spectra of Ag-Au alloy metal nanorods as a function of Ag concentration. It is observed that the sensitivity does not depend on the type of the metal but depends largely on the aspect ratio of nanorods. The direct dependence of the sensitivity on the aspect ratio becomes more prominent as the size of nanorods becomes larger. However, the use of larger nanoparticles may induce an excessive broadening of the resonance spectrum due to an increase in the contribution of multipolar excitations. This restricts the sensing resolution. The insensitivity of the plasmon response to the metal composition is attributable to the fact that the bulk plasma frequency of the metal, which determines the spectral dispersion of the real dielectric function of metals and the surface plasmon resonance condition, has a similar value for the noble metals. On the other hand, nanorods with higher Ag concentration show a great enhancement in magnitude and sharpness of the plasmon resonance band, which gives better sensing resolution despite similar plasmon response. Furthermore, Ag nanorods have an additional advantage as better scatterers compared with Au nanorods of the same size.

5. Prashant K. Jain, Susie Eustis, Mostafa A. El-Sayed, "Plasmon Coupling in Nanorod Assemblies: Optical Absorption, Discrete Dipole Approximation Simulation, and Exciton-Coupling Model," *Journal of Physical Chemistry B*, 110(37), 18243-18253, (2006).

Abstract: The shape anisotropy of nanorods gives rise to two distinct orientational modes by which nanorods can be assembled, i.e., end-to-end and side-by-side, analogous to the well-known *H* and *J* aggregation in organic chromophores. Optical absorption spectra of gold nanorods have earlier been observed to show a redshift of the longitudinal plasmon band for the end-to-end linkage of nanorods, resulting from the plasmon coupling between neighboring nanoparticles, similar to the assembly of gold nanospheres. We observe, however, that side-by-side linkage of nanorods in solution shows a blue-shift of the longitudinal plasmon band and a redshift of the transverse plasmon band. Optical spectra calculated using the discrete dipole approximation method were used to simulate plasmon coupling in assembled nanorod dimers. The longitudinal plasmon band is found to shift to lower energies for end-to-end assembly, but a shift to higher energies is found for the side-by-side orientation, in agreement with the optical absorption experiments. The strength of plasmon coupling was seen to increase with decreasing inter-nanorod distance and an increase in the number of interacting nanorods. For both side-by-side and end-to-end assemblies, the strength of the longitudinal plasmon coupling increases with increasing nanorod aspect ratio as a result of the increasing dipole moment of the longitudinal plasmon. For both the side-by-side and end-to-end

orientation, the simulation of a dimer of nanorods having dissimilar aspect ratios showed a longitudinal plasmon resonance with both a blue-shifted and a red-shifted component, as a result of symmetry breaking. A similar result is observed for a pair of similar aspect ratio nanorods assembled in a nonparallel orientation. The inter-nanorod plasmon coupling scheme concluded from the experimental results and simulations is found to be qualitatively consistent with the molecular exciton coupling theory, which has been used to describe the optical spectra of *H* and *J* aggregates of organic molecules. The coupled nanorod plasmons are also suggested to be electromagnetic analogues of molecular orbitals. Investigation of the plasmon coupling in assembled nanorods is important for the characterization of optical excitations and plasmon propagation in these nanostructures. The surface plasmon resonance shift resulting from nanorod assembly also offers a promising alternative for analyte-sensing assays.

6. Alexander W. Schill, Christopher S. Gaddis, Wei Qian, Mostafa A. El-Sayed, Ye Cai, Valerie T. Milam, Kenneth Sandhage, "Ultrafast Electronic Relaxation and Charge-Carrier Localization in CdS/CdSe/CdS Quantum-Dot Quantum-Well Heterostructures," Nano Letters, 6(9), 1940-1949, (2006).

Abstract: The relaxation and localization times of excited electrons in CdS/CdSe/CdS colloidal quantum wells were measured using sub-picosecond spectroscopy. HRTEM analysis and steady-state PL demonstrate a narrow size distribution of 5-6 nm epitaxial crystallites. By monitoring the rise time of the stimulated emission as a function of pump intensity, the relaxation times of the electron from the CdS core into the CdSe well are determined and assigned. Two-component rise times in the stimulated emission are attributed to intraband relaxation of carriers generated directly within the CdSe well (fast component) and charge transfer of core-localized carriers across the CdS/CdSe interface (slow component). This is the first reported observation of simultaneous photon absorption in the core and well of a quantum-dot heterostructure. With increasing pump intensity, the charge-transfer channel between the CdS core CdSe well contributes less to the stimulated emission signal because of filling and saturation of the CdSe well state, making the interfacial charge-transfer component less efficient. The interfacial charge-transfer time of the excited electron was determined from the slow component of the stimulated emission build-up time and is found to have a value of 1.2 ps.

7. Wenyu Huang, Wei Qian and Mostafa A. El-Sayed, "Gold Nanoparticles Propulsion from Surface Fueled by Absorption of Femtosecond Laser Pulse at Their Surface Plasmon Resonance," Journal of the American Chemical Society, 128(41), 13330- 13331, (2006).

THIS IS A COMMUNICATION SO THERE IS NO ABSTRACT BUT ONE PARAGRAPH IN THE PAPER SUMMARIZES THE WORK AS FOLLOWS:

In the present communication, we report on the observation that, when femtosecond laser pulses in resonance with the strong surface plasmon oscillations are used for excitation, the rates of absorption and heating become faster than the rate of melting of the nanoparticle. The nanoprism is observed to fly away while preserving its shape. SEM

shows that it has a reduced bisector, and AFM study shows that its thickness is also reduced. Furthermore, it is observed that the sizes of the nanoparticles that are displaced from their original position are smaller than the space they occupied prior to their exposure to the laser pulses. Of the different mechanisms discussed, only the gold atom sublimation mechanism can account for these observations. The gold rapid sublimation could result in a rapid build up of an ultrahigh gold atomic pressure underneath the prism, which enables it to fly. Making few approximations, we calculate an average velocity of 160 m/s for the propelled nanoparticle that is irradiated under laser intensity of 5.1 mJ/cm².

Different Grant No: 0527297:

8. Qusai Darugar, Wei Qian, and Mostafa A. El-Sayed, "Observation of optical gain in solutions of CdS quantum dots at room temperature in the blue region," *Applied Physics Letters*, 88, 261108, (2006).

Abstract: The optical gain dynamics has been studied for two CdS quantum dot samples dispersed in toluene at room temperature. This was carried out by using femtosecond transient absorption technique with an excitation at 400 nm and gain measurement was studied at the fluorescence maxima (440 and 460 nm). The optical gain lifetime was found to be as long as 20 ps under pump fluence as low as 0.77 mJ/cm². The low threshold is the result of long lifetime of electrons and holes and narrow emission bandwidth. These results suggest that CdS quantum dots in solution are excellent gain media for optically pumped high power blue lasers.

2007

1. Tabor, Christopher; Qian, Wei; El-Sayed, Mostafa A. "Dependence of the Threshold Energy of Femtosecond Laser Ejection of Gold Nanoprisms from Quartz Substrates on the Nanoparticle Environment," *Journal of Physical Chemistry C*, 111(25), 8934-8941, (2007).

Abstract: Recently, it was reported that gold nanoprisms in a monolayer array on a quartz substrate were ejected in air when irradiated with femtosecond laser pulses near their surface plasmon absorption maximum. It was deduced from the measured reduction in particle thickness upon irradiation that the ejection mechanism involved ablation of surface atoms from the gold particle, which generates an intense pressure at the particle-substrate interface. The present study reports on this phenomenon when the substrate-bound nanoparticle is immersed in a liquid environment. In this system, it is found that the nanoparticle ejection requires less than one tenth the energy required if the system was irradiated in air. The ejected nanoparticle is also found to increase in thickness instead of the decrease observed in air. These results suggest another photoinitiated ejection mechanism, different from surface ablation, when the particles are surrounded by a liquid environment. From this and other spectroscopic and microscopic results on the ejected nanoprisms, we suggest a mechanism that involves energy transfer from the

photoexcited nanoprism to the solvent within cavities and defects at the particle-substrate interface. The hot-solvent molecules result in an intense pressure at the particle-substrate interface, resulting in particle ejection. Ejection is proposed to consist of two processes, namely nanoparticle-substrate dissociation and nanoparticle solvation and diffusion away from the substrate. These two processes have independently been studied as a function of solvent property.

2. Nishikiori, Hiromasa; Qian, Wei; El-Sayed, Mostafa A.; Tanaka, Nobuaki; Fujii, Tsuneo. "Change in Titania Structure from Amorphousness to Crystalline Increasing Photoinduced Electron-Transfer Rate in Dye-Titania System," Journal of Physical Chemistry C, 111(26), 9008-9011, (2007).

Abstract: Thin titania gel films containing well-dispersed fluorescein dye were prepared by the sol-gel method and treated with steam to promote crystal growth of the titania particles. It is known that steam treatment converts the titania structure from amorphousness to crystalline. In the present study, such change is found to increase the rate of the photoinduced electron transfer from and to dispersed fluorescein dye